ADSORPTION ON CHROMITE CATALYSTS

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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C. G ALBERT

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ADSORPTION ON CHROMITE CATALYSTS

The close relation between the adsorption of gases by solids and contact catalysis is quite generally accepted, and has been much discussed in the literature. In this laboratory the chromites have been thoroughly studied as catalysts for the oxidation of carbon monoxide by Lory (5) and later by Lockwood (4). This suggested that a detailed study of the adsorption by chromite catalysts of carbon monoxide and oxygen, paying particular attention to the so-called "activated adsorption," would not be without interest and value in shedding more light on the question of the relation between adsorption and catalytic activity.

If adsorption does play a major part in contact catalysis, it is certainly this high-temperature variety, with its "energy of activation," which must be considered. For, as Garner pointed out (3), when Taylor (7) described the phenomenon in 1931, he suggested the term "activated adsorption" merely to indicate that the process taking place was one which involved a temperature coefficient, although the fact that it occurs at the temperatures at which the surface under consideration is catalytically active might be construed as indicating that the term might equally well have been used to mean that the adsorbed molecules are in some active state.

Since the surface of the chromite catalyst under consideration is catalytically active for the combination of carbon monoxide and oxygen at temperatures of 100–200°C., its adsorption of both of these gases was studied over this range in temperature, noting particularly the rate at which the adsorption process takes place. The purpose of the investigation was to measure the extent to which the adsorption takes place, and also to obtain sufficient data on its rate to permit the calculation of the energy of activation associated with the process in each case.

APPARATUS

The apparatus used in making these measurements was essentially the same as that described by McKinney (6) and used also by Taylor and

Strother (8). Like McKinney's apparatus, it was so designed as to permit the measurement of adsorption at constant pressure, with its rate, and also to measure the adsorption at constant volume in order to plot the isothermals.

The gas buret used in these measurements was graduated in hundredths of a cubic centimeter, and the distance between these graduations was over a millimeter,—large enough so that fractions of a division could be estimated with considerable accuracy. The buret was surrounded by a water jacket through which a constant stream of small bubbles of air was kept flowing in order to insure uniformity of temperature along the length of the buret. A thermometer, graduated in fifths of a degree, was suspended in the water jacket, and the temperature was recorded each time a reading was made.

THE CATALYST

The sample of copper chromite used in the adsorption measurements was the Copper Chromite No. 1 prepared and tested for its efficiency by Lockwood (4). At the conclusion of the adsorption measurements, the catalyst was again tested, using the same apparatus used by Lockwood. The results obtained were, within a reasonable experimental error, the same as those of Lockwood, which are summarized in table 1.

TABLE 1

Efficiency of copper chromite No. 1 after the adsorption measurements

TEMPERATURE	CONVERSION
°C.	*per cent*
139	40
166	85
181	100

MATERIALS

The gases used in the adsorption measurements were very carefully purified before being placed in their storage bulbs. Each gas was passed through its purification train for at least an hour, in order to sweep out the air, before being admitted to the system.

EXPERIMENTAL RESULTS

Adsorption of oxygen at constant pressure

The adsorption of oxygen at a pressure of 350 mm. Hg was studied at temperatures covering the range over which the activity of copper chromite as a catalyst for the air oxidation of carbon monoxide varies from prac-

tically no activity at all to 100 per cent conversion of carbon monoxide to carbon dioxide.

In order to make the results at different temperatures comparable, the catalyst was heated, before each run, to 300°C. under 400 mm. Hg of

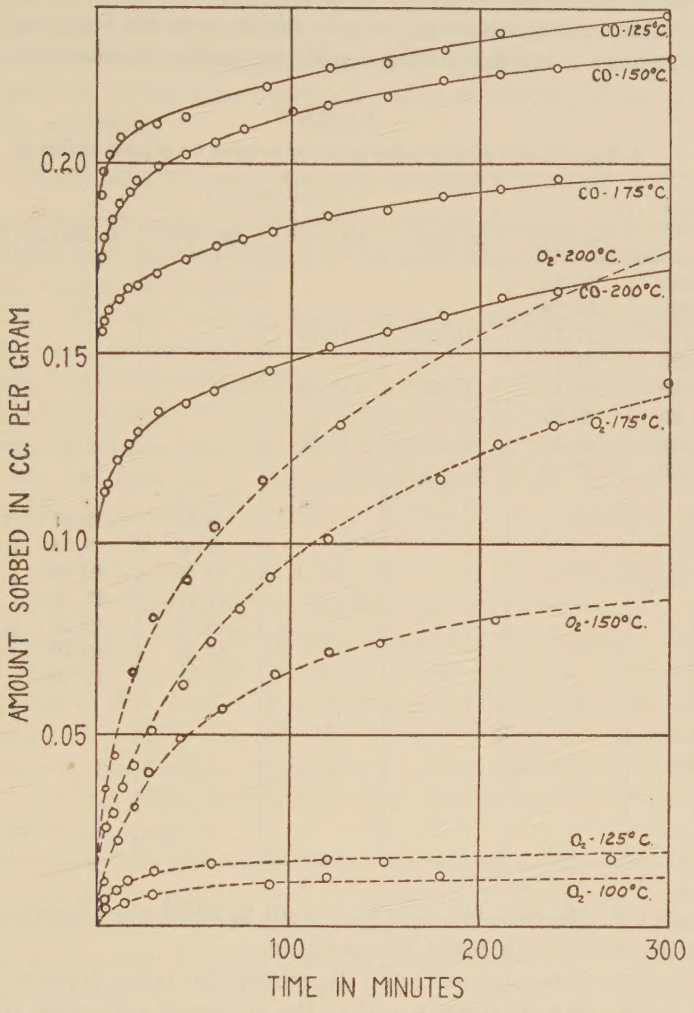

FIG. 1. Adsorption of carbon monoxide and oxygen on copper chromite at 350 mm. of mercury

carbon monoxide, and then thoroughly evacuated. Lory (5) states that any surface chromate formed is reduced by carbon monoxide at 100°C. The treatment given the catalyst, then, should surely prevent any chromate formed during the previous run from interfering with the results. All of

the runs were checked several times, and the curves obtained could be duplicated within about 2 per cent. The data on the adsorption of oxygen are represented graphically in figure 1.

It is evident from the figure that the adsorption of oxygen at these temperatures exhibits the one chief characteristic of activated adsorption to which Taylor called attention,—a rate which, over the temperature range studied, shows a marked increase with increasing temperature. In this

TABLE 2

Activation energies of adsorption of oxygen on copper chromite

AMOUNT ADSORBED	E (IN KG-CAL.)					
	100–125°C.	100–150°C.	125–150°C.	150–175°C.	150–200°C.	175–200°C.
0.00500	15.43					
0.00625	15.78					
0.00750	17.41	16.19	14.79			
0.00875	17.71					
0.01000	19.11	17.50	15.66			
0.01125	20.51					
0.01250	25.51	22.62	18.66			
0.01500	22.04					
0.03				9.59	9.31	8.99
0.04				9.46	9.54	9.63
0.05				10.19	10.29	10.40
0.06				11.76	11.53	11.28
0.07				13.07	12.29	11.41
0.08				16.50	13.79	10.76
0.09					17.19	10.61
0.10						10.89
0.11						10.96
0.12						11.03
0.13						11.61
0.14						12.72
0.15						15.64

case, not only the rate, but also the extent to which the adsorption occurs, increases greatly with rising temperature.

If, at two temperatures T_1 and T_2, adsorption takes place to the same extent in the time intervals t_1 and t_2, the energy of activation to be associated with the adsorption process over that temperature interval may be calculated from the equation

$$\ln \frac{t_2}{t_1} = \frac{E}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Calculating, with this equation, the energy of activation, E, from the

data illustrated in figure 1 on the adsorption of oxygen at constant presssure by copper chromite, we obtain the values for E listed in table 2.

The fact that the activation energies for the lower temperature ranges come out considerably higher than those at somewhat higher temperatures is due to the fact that the calculations at the lower temperatures involve a much more nearly saturated surface, since the total amount of adsorption which takes place at these temperatures is so much less. At the higher temperatures, the energy of activation is rising to similar values as more of the gas is adsorbed.

Adsorption of carbon monoxide at constant pressure

The adsorption of carbon monoxide on copper chromite at a constant pressure of 350 mm. Hg was studied at the same temperatures used in the study of the oxygen adsorption.

A great deal has been written, particularly by Burrage (2), about the importance, when comparing the rates of reaction found in different runs, of being certain that the surface of the absorbent was in the same condition at the start of each run. When each carbon monoxide run was made after simply pumping off the gas from the previous run at the temperature at which the run had been made, the results obtained could not be checked and appeared to be without meaning. Evidently the condition of the catalyst surface at the beginning of a run varied considerably, according to whether the previous run had been made at a temperature higher or lower than that at which the succeeding run was to be made.

It was decided to make a set of runs after giving the catalyst a definite treatment, the same treatment being used before each run. The catalyst was first heated to 275–300°C. for an hour under a definite pressure of carbon monoxide. Then the catalyst was thoroughly degassed, and allowed to cool down to the desired temperature. Runs made in this manner could be checked to within 2 to 5 per cent. A set of data from such runs is shown graphically in figure 1.

These runs, in which the condition of the catalyst surface should have been about the same, indicate that the amount of adsorption is less the greater the temperature. Obviously, it is impossible to apply the formula used before to the data of figure 1 and to calculate energies of activation. It is apparent, however, that the order in which the curves fall is determined by the amount of instantaneous adsorption.

This part of the adsorption has the characteristics of van der Waals adsorption. Benton (1) stated that in most cases the van der Waals adsorption disappeared at about 200°C. above the boiling point of the gas. However, he found a type of adsorption which showed the speed characteristic of the van der Waals adsorption with carbon monoxide on copper at 110°C., while the boiling point of carbon monoxide is −192°C. The

van der Waals adsorption in the case of carbon monoxide on copper chromite appears to be prominent even at a temperature nearly 400°C. above the boiling point of the carbon monoxide, as is shown by the 0.11 cc. per gram adsorbed instantaneously at 200°C. A brief run was made at 300°C., and the 1-minute reading at this temperature, in cc. per gram, was 0.03, the curve starting out similarly to those for oxygen at the lower temperatures. This would indicate that finally, 500°C. above the boiling point of the carbon monoxide, the van der Waals adsorption is disappearing from the picture.

If we take the 1-minute reading for each of the carbon monoxide runs, whatever it may be, as zero, and plot the amount adsorbed over and above this fixed quantity against time, curves like those in figure 2 are obtained.

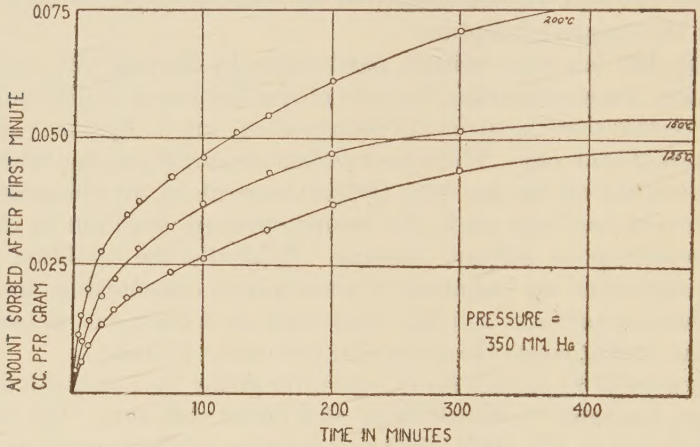

FIG. 2. Activated adsorption of carbon monoxide on copper chromite

These curves are similar to those for oxygen, and are suitable for the calculation of energies of activation.

Since the amounts adsorbed used in plotting the original adsorption versus time curves of figure 1 are obtained by subtracting one experimental value from another nearly the same size, the percentage error in the reading is greatly multiplied by the time the adsorption curves are obtained. The final curves, those of figure 2, are obtained by repeating the process of subtracting one value from another very nearly the same size. Thus the original numbers (the volumes read on the gas buret) have now shrunk to new values numerically only about one-fiftieth of the size of the original ones, and it is to be expected that as a consequence of this the percentage errors will have grown to large proportions.

Nevertheless, it is possible to take these last curves of figure 2 and to calculate from them fairly consistent energies of activation, although the

agreement is quite naturally not nearly as good as in the case of the adsorption of oxygen at constant pressure. Some of the calculations of energies of activation are summarized in table 3.

The rapidity with which a considerable amount of carbon monoxide is adsorbed on the chromite suggested that perhaps something approximating a monomolecular layer is formed at once, and that the "activated" adsorption consists of building up a thicker layer.

TABLE 3

Energies of activation: carbon monoxide on copper chromite

AMOUNT ADSORBED	E (IN KG-CAL.)		
	125–150°C.	125–200°C.	150–200°C.
0.0100	8.17		
0.0125	7.92		
0.0150	9.34		
0.0175	10.11		
0.0200	11.06	8.61	7.16
0.0225	11.29	8.64	7.07
0.0250	11.74	8.45	6.49
0.0275	11.38	8.42	6.67
0.0300	10.42	8.28	7.01
0.0325	9.70	7.83	6.71

TABLE 4

Carbon monoxide adsorption in the first minute

TEMPERATURE	ADSORPTION
°C.	*atoms per gram*
100	5.54×10^{18}
125	5.26×10^{18}
150	4.75×10^{18}
175	4.16×10^{18}
200	2.76×10^{18}

Lory (5) studied the amount of chromate that could be leached off samples of various chromites with water, after the chromites had been heated in the air to form a surface layer of the chromate. From the data which he obtained in this manner, he calculated the number of chromium atoms on the surface of the catalyst. For copper chromite he obtained the value 4.11×10^{18} atoms of chromium on the surface for each gram of the catalyst.

The sample of copper chromite used in these measurements was prepared by following Lory's method to the smallest detail, and may be assumed to have approximately the same number of surface chromium atoms. If we assume that the adsorption takes place on the chromium atoms, then a

monomolecular layer must be considered as one molecule of carbon monoxide to each surface chromium atom, or about 4.11×10^{18} atoms per gram. The observed amounts of carbon monoxide adsorption in the first minute, converted from cubic centimeters per gram to atoms per gram are given in table 4. Obviously, the amount of this rapid adsorption is, at the temperatures studied, of the same order of magnitude as that required to form a monomolecular layer on the surface of the catalyst.

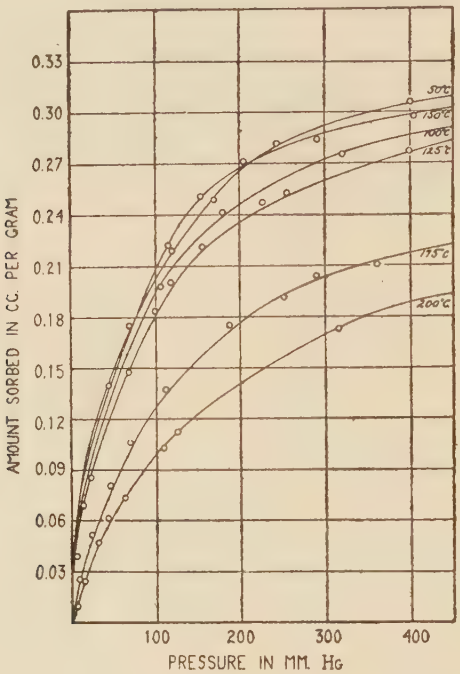

FIG. 3. Adsorption of carbon monoxide on copper chromite at constant volume

Adsorption of carbon monoxide at constant volume

The different character of the adsorption versus time curves for carbon monoxide, as compared with those for oxygen, suggested that the processes taking place were not of the same nature.

In order to obtain a better understanding of the question of the adsorption of carbon monoxide, it was considered worth while to obtain the data necessary to plot the isotherms for the adsorption of carbon monoxide,—the total adsorption of all kinds when equilibrium had been reached. With this in mind, constant volume runs were made at seven temperatures, covering the entire range where the catalyst is active. The data thus obtained are shown graphically in figure 3.

DISCUSSION

The adsorption of oxygen by copper chromite appears to be a straightforward process. It seems probable that it is simply a chemical reaction, that of surface chromate formation. At the temperature range over which the adsorption was studied, which is the important range as regards catalysis, the activated adsorption is the only process taking place, so that there are no complications introduced by concurrent reactions.

The case of the adsorption of carbon monoxide on copper chromite is not so simple. Two adsorption processes combine to give the observed results, and it is only by separating the two and considering each one individually that we can obtain any understanding of either one. The curves

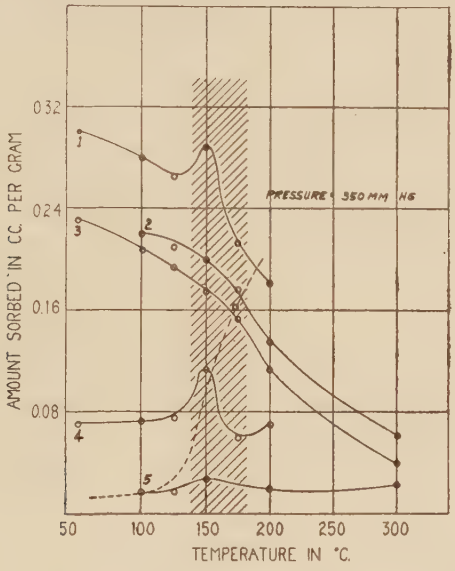

FIG. 4. Summary of carbon monoxide adsorption

of figure 4 represent both the sum of the van der Waals and the activated adsorption, and each one separately. Considering only the one pressure used throughout the rate measurements, 350 mm. Hg, curve 1 is taken from the isotherms in figure 3, and shows the total amount adsorbed at equilibrium at this pressure and at each of the temperatures considered. These amounts diminish regularly with increasing temperature except in the neighborhood of 150°C., where a sharp maximum is observed. It would be expected that this maximum, coming at such a high temperature, would be due to the activated adsorption rather than to the van der Waals variety.

Curve 3, which shows the 1-minute readings from the constant pressure

runs, bears out this expectation. This curve may be taken as representing the van der Waals adsorption alone at each of the temperatures. Evidently this type of adsorption falls off rapidly with rising temperatures, and exhibits no maxima or minima.

The difference between curves 1 and 3, then, must obviously represent the total *amount* of activated adsorption which takes place. This is represented graphically in curve 4, and the maximum in the region of 150°C. is very pronounced. The temperature range in which the catalytic efficiency of the chromite in assisting the combination of carbon monoxide and oxygen rises from about 40 per cent to 100 per cent is shown by the shaded area. In this range of temperature the amount of activated adsorption is considerably less than the amount of van der Waals adsorption, although it appears likely that this condition will be reversed at a somewhat higher temperature.

Curve 2 is the representation of the 30-minute readings taken from the curves of figure 1. The difference, then, between this curve and curve 3 will be the amount adsorbed at each temperature in the interval from one to thirty minutes, and will be proportional to the *rate* of the activated adsorption. This difference is represented by curve 5. It is evident that there is a maximum in the rate of the activated adsorption at about the same temperature at which we find the maximum in the extent to which it takes place.

These maxima in the amount of activated adsorption and in its rate suggest that perhaps there are two distinctly separate and entirely different processes taking place at the surface in addition to the van der Waals adsorption, which, for the moment, we are neglecting. Both of these processes, of course, would be included in a general definition of adsorption as any way in which a gas is taken up by a solid. But although each takes place at a measurable rate, the amount of one falls off with rising temperatures, whereas on the contrary, the amount of the other becomes greater as the temperature becomes higher.

In figure 5a the solid line curve is a duplicate of curve 4 in figure 4. Similarly, in figure 5b the solid curve is a duplicate of curve 5 in figure 4. In each case the broken-line curves marked a and b are arbitrarily drawn, regular curves which, when added together, give the curves with the maxima.

It does not seem wholly improbable that what we have been considering, then, as the activated adsorption of carbon monoxide on the chromite surface might possibly be really the summation of two distinctly separate processes, which, although in no sense do they work at cross purposes, nevertheless vary in a different way with temperature. These two processes, if such exist, could then be represented by curves of the type of those drawn in broken lines in figures 5a and 5b.

In figure 5a these curves will represent the extent to which these processes take place before equilibrium is reached at a pressure of 350 mm. Hg and the temperatures indicated, while the curves of figure 5b would be proportional to the rates at which the processes take place.

If we may represent the adsorption as the sum of two such hypothetical processes, one of them, that represented by b, diminishes with rising temperature, not only as regards the extent to which it occurs, but also in the rate at which it takes place.

It must be remembered that the differences between the adsorption curves for carbon monoxide are not large in comparison with the values involved. It may be possible that experimental errors are responsible for the maxima obtained in figures 4 and 5. However, the fact that the

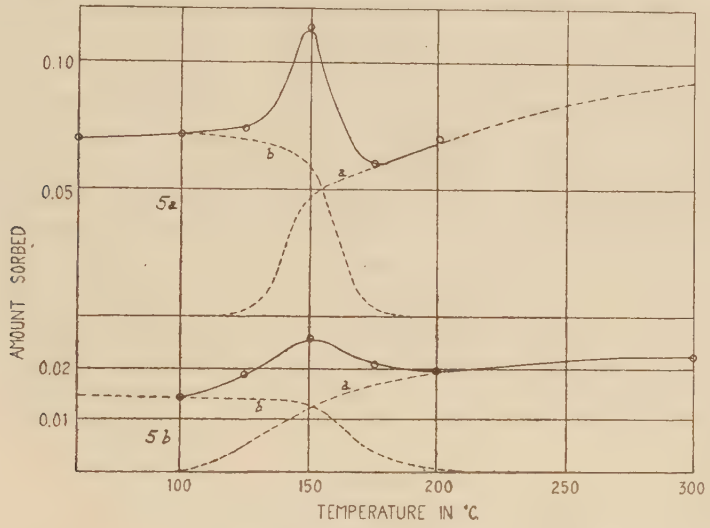

FIG. 5. Activated adsorption of carbon monoxide

maxima occur in the same temperature interval in each case and are so similar appears to bring the hypothetical processes suggested into the realm of possibility. If they do exist, perhaps one of the processes is one of solution, or diffusion, or some such phenomenon. At any rate, the exact nature of the two processes is of no importance as regards the relation of the adsorption process to catalytic activity, as we shall see directly.

In the range over which the efficiency of the chromite as a catalyst for the oxidation of carbon monoxide nears 100 per cent, the adsorption of carbon monoxide is falling off rapidly from its maximum, which makes it seem doubtful that it is of major importance in the mechanism of the catalytic reaction.

As the temperature is increased over this range, however, the adsorption

of oxygen rises extremely rapidly. It seems more likely, then, that the determining factor in the activity of the surface is the adsorption of oxygen. A suggested mechanism which seems reasonable is that the oxygen is first adsorbed on the chromite surface with an energy of activation of the order of those calculated. If the temperature is high enough so that the adsorption of the oxygen reaches sufficient proportions, any carbon monoxide passing over the catalyst surface either reacts directly with the adsorbed oxygen, or else is first adsorbed and then reacts, after which the carbon dioxide produced is desorbed.

Lory suggested that the catalytic activity was due to alternate oxidation of the chromite surface by oxygen and its reduction by carbon monoxide. If the term "adsorption" is defined as including *all ways* in which a gas is taken up at a solid surface, without regard to the nature of the binding between the surface and the adsorbed gas, adsorption would of course include the oxidation of the surface chromium atoms by gaseous oxygen. So in the strictest sense there is no real difference between the suggested mechanism and that proposed by Lory.

However, since the oxidation of the chromite is probably a process involving the addition of oxygen to the *surface* chromium atoms only, it seems wise to speak of it as an adsorption process, thus emphasizing the fact that it is a surface phenomenon,—for the surface is all-important in contact catalysis. At least, until it may be shown that the binding of the adsorbed gas to the surface is identical with that between atoms of the surface material and of the gas in their known compounds, it appears more to the point to use the term "adsorption" rather than "oxidation" to describe the process.

REFERENCES

(1) Benton, A. F.: Trans. Faraday Soc. **28**, 202 (1932).
(2) Burrage, L. J.: Trans. Faraday Soc. **28**, 192–4 (1932).
Burrage, L. J.: Trans. Faraday Soc. **29**, 677–8 (1933).
(3) Garner, W. E.: Trans. Faraday Soc. **28**, 261 (1932).
(4) Lockwood, W. H.: J. Phys. Chem. **38**, 735–46 (1934).
(5) Lory, E. C.: J. Phys. Chem. **37**, 685–92 (1933).
(6) McKinney, Paul: J. Phys. Chem. **37**, 381 (1933).
(7) Taylor, H. S.: J. Am. Chem. Soc. **53**, 578–97 (1931).
(8) Taylor, H. S., and Strother, C. O.: J. Am. Chem. Soc. **56**, 586–91 (1934).

BIOGRAPHY

The author was born in Piper City, Illinois, on April 3, 1911. He received his elementary education in the public schools of Pueblo, Colorado and Sigourney, Iowa. While a sophomore in the Sheffield Scientific School of Yale University he was awarded the Mary Carroll Garvan Fellowship to study at Johns Hopkins. He entered the Johns Hopkins University in September, 1931, and received his Ph.D. degree in June, 1935.